Chemistry

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Chemical Equilibrium

Outline:

- Reversible and irreversible reactions
- State of chemical equilibrium
- Equilibrium constant expression for important reaction
- Applications of equilibrium constant
- Le-Chatelier's principle
- Synthesis of ammonia by Haber's process
- Common ion effect
- Buffer solutions
- Equilibrium of slightly soluble ionic compounds (solubility product)

Chemical Equilibrium

Irreversible Reaction ($\rightarrow$)	Reversible Reaction ($\rightleftharpoons$)
Takes place in only one direction under standard conditions	Takes place in both directions i.e. forward and reverse under standard conditions
Goes to completion	Never goes to completion
No equilibrium state occurs	Equilibrium state is the ultimate goal
Can be carried out in open as well as in closed container	Only carried out in closed container

Chemical Equilibrium:

- State or position of system at which rate of forward reaction is equal to rate of reverse reaction is called dynamic equilibrium
  - It is macroscopic property (deals with molecules in bulk)
  - At start reactant are higher in concentration and concentration decreases as reaction proceeds until becomes constant at equilibrium
  - At start conc. of product is zero, it increases as reaction proceeds until becomes constant at equilibrium
  - Equilibrium can be initiated from either side
  - A catalyst cannot change equilibrium state
  - At equilibrium, concentration of various species remain constant

Types of Chemical Equilibrium

- **Homogeneous:** Reactant and Product are in same phase
- **Heterogeneous:** Reactant and Product are in different phase

Law of Mass Action:

- Rate of reaction (whether forward or reverse) is directly proportional to active masses of reactants (raised to power exponents)
- For dilute solutions; Active masses are equal to concentrations [ ]
- Unit of concentration is mole dm^{-3}

$$aA + bB \underset{K_r}{\overset{K_f}{\rightleftharpoons}} cC + dD$$

$$R_f \propto [A]^a [B]^b \quad ⋙ \quad R_f = k_f [A]^a [B]^b$$

$$R_r \propto [C]^c [D]^d \quad ⋙ \quad R_r = k_r [C]^c [D]^d$$

- At Equilibrium;

$$R_f = R_r$$

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

$$K_c = \frac{K_f}{K_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[\text{Product}]}{[\text{Reactant}]}$$

- K_f, k_r are specific rate constants of forward and reverse reactions respectively
- K_c is equilibrium constant

Features of K_c: (Example.1,3)

- May or may not have unit
- Independent of concentration, pressure/volume and catalyst
- Affected by temperature, nature of reactants
- K_c is thermodynamic property associated with enthalpy
- In fact all equilibrium constants are only affected by temperature

Unit of K_c:

- When $n_R = n_P$, K_c has no unit

$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(\text{mole dm}^{-3})(\text{mole dm}^{-3})}{(\text{mole dm}^{-3})(\text{mole dm}^{-3})} = \text{No unit}$$

- When $n_R \neq n_P$, K_c has unit; $[(\text{moledm}^{-3})^{\Delta n}]$ $\quad\quad \Delta n = n_P - n_r$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(\text{mole dm}^{-3})^2}{(\text{mole dm}^{-3})(\text{mole dm}^{-3})^3} = \text{mole}^{-2}\ \text{dm}^6$$

K_c Expression for various Reactions: [Q.8, Q.19,20 (for concept)]

1.

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial	a moles		b moles		0 moles
At equilibrium	(a-x) moles		(b-3x) moles		(0+2x) moles

For concentration, divide all by volume

$$\frac{(a-x)}{V} \quad\quad \frac{(b-3x)}{V} \quad\quad \frac{(2x)}{V}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x/V)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

2.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial	a moles		0 moles		0 moles
At equilibrium	(a-x) moles		(0+x) moles		(0+x) moles

For concentration, divide all by volume

$$\frac{(a-x)}{V} \qquad \frac{(x)}{V} \qquad \frac{(x)}{V}$$

$$K_c = \frac{[PCl_3]^1[Cl_2]^1}{[PCl_5]^1} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{V(a-x)}$$

3. $CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$ ⋙ $K_c = \frac{x^2}{(a-x)(b-x)}$

Equilibrium Terms:

- K_c = Equilibrium constant in terms of concentration
- K_p = Equilibrium constant in terms of partial pressure of gases
- K_n = Equilibrium constant in terms of no. of moles
- K_x = Equilibrium constant in terms of mole fraction

$$aA + bB \underset{K_r}{\overset{K_f}{\rightleftharpoons}} cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b},\ K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b},\ K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b},\ K_x = \frac{X_C^c \times X_D^d}{X_A^a \times X_B^b}$$

- **Relationship b/w K_c & K_p:** $\boldsymbol{K_p = K_c (RT)^{\Delta n}}$ ($\Delta n = n_{product} - n_{reactant}$)
  1. If $n_P = n_R$ ⇒ $K_p = K_c$
  2. If $n_P > n_R$ ⇒ $K_p > K_c$
  3. If $n_P < n_R$ ⇒ $K_p < K_c$

  Example#2: N_2 and H_2 combine to give NH_3. The value of K_c in this reaction at 500°C is 6.0×10^{-2}. Calculate the value of K_p for this reaction

  Solution:

  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta n = n_P - n_R = 2 - 4 = -2$)

  T = 500 + 273 = 773 K R = 0.0821 $atmdm^3mol^{-1}K^{-1}$

  $K_p = 6.0 \times 10^{-2} (0.0821 \times 773)^{-2}$

  $\boldsymbol{K_p = 1.5 \times 10^{-5}}$ ($K_p < K_c$)

- **Applications of K_c:**
  1. **Direction of Reaction:** $Q_c = \frac{[Product]}{[Reactant]}$
     - $Q_c = K_c$ ⇒ Equilibrium state
     - $Q_c > K_c$ ⇒ Reverse direction to attain equilibrium
     - $Q_c < K_c$ ⇒ Forward direction to attain equilibrium
  2. **Extent of Reaction:**

- ☞ K_c is very large
  - Almost completes in forward direction

    $2O_3 \rightleftharpoons 3O_2$ $K_c = 10^{55}$ at 25^0C

    $H_2 + Br_2 \rightleftharpoons 2HBr$ $K_c = 5.4 \times 10^{18}$ at 25^0C
  - Reactants are unstable (very less stable) and products are stable
- ☞ K_c is moderate (small)
  - Does not proceed appreciably in forward direction

    $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $K_c = 10$ at 25^0C

    $CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$ $K_c = 4$ at 25^0C

    $N_2O_4 \rightleftharpoons 2NO_2$ $K_c = 0.36$ at 25^0C
  - Reactants and products are almost equally stable
- ☞ K_c is very small
  - Very little forward reaction

    $2HF \rightleftharpoons H_2 + F_2$ $K_c = 10^{-13}$ at 2000^0C

    $N_2 + O_2 \rightleftharpoons 2NO$ $K_c = 1 \times 10^{-30}$ at 25^0C
  - Products are unstable (very less stable) and reactants are stable

3. The Effect of Conditions on the Position of Equilibrium

- ☞ Will be discussed in Le-Chatelier's principle

Le-Chatelier's Principle

- ✓ If a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress
- ✓ Applicable on both physical and chemical changes

1. Effect of change in Concentration:

- Increase in conc. of reactant or decrease in conc. of product ⇒ Forward
- Decrease in conc. of reactant or Increase in conc. of product ⇒ Reverse

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

- Formation of 'BiOCl'(insoluble ppts) makes the solution cloudy
- If we add HCl (product), the reaction moves backwards and we get clear solution
- If we add H_2O (reactant), the reaction moves forward and we get more cloudy solution

2. Effect of change in Pressure/Volume: (Remember $P \propto \frac{1}{V}$)

- Pressure/volume only affects gaseous reactions in which $n_P \neq n_R$
- Increase in pressure favours the reaction towards lesser no. of moles (or direction in which moles are decreasing
- $2SO_2 + O_2 \rightleftharpoons 2SO_3$ Increase in pressure moves it in forward (as going in forward direction moles are decreasing)

$n_R > n_P$	$n_R < n_P$
Increase in 'P' shifts the reaction forward	Increase in 'P' shifts the reaction backwards
Decrease in 'P' shifts the reaction backwards	Decrease in 'P' shifts the reaction forward

3. Effect of change in Temperature:

- In reversible reactions; if reaction is exothermic in forward direction, it will be endothermic in reverse direction or vice versa

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = -92.46\ kj$$

- This reaction will be exothermic in forward direction and so endothermic in reverse direction
- Increase in temperature favours the Endothermic reaction (moves the reaction in direction in which it is endothermic)
- Decrease in temperature favours the Exothermic reaction (moves the reaction in direction in which it is exothermic)
- **For endothermic reaction in forward**, increase in 'T' increases rate of reaction, increases the amount of product formed (yield) and K_c value increases
  Decrease in 'T' decreases rate of reaction and decreases the amount of product formed (yield) and K_c value decreases
- **For exothermic reaction in forward**, increase in 'T' increases rate of reaction, decreases the amount of product formed (yield) and K_c value decreases
  Decrease in 'T' decreases rate of reaction and increases the amount of product formed (yield) and K_c value increases
- **Effect of 'T' on solubility:**
  - Glucose, sucrose, NH_4Cl, KI, KBr etc have positive enthalpy of solution (endothermic solubility), so increase in 'T' will increase their solubility
  - Li_2CO_3, Na_2CO_3, LiCl, $Ce_2(SO_4)_3$, LiBr etc have negative enthalpy of solution (exothermic solubility), so increase in 'T' will decrease their solubility and increase their precipitation
  - Solubility of salts with enthalpy of solution nearly zero or zero is not affected by change in temperature like for NaCl

4. Effect of Catalyst:

- A catalyst neither affects equilibrium position nor equilibrium constant but increases rate of both forward and reverse reactions equally by providing new path (lowering the activation energy)

Haber's Process for Ammonia Synthesis

- Nitrogen is taken from the air (nearly 13 % nitrogen fixation)
- Hydrogen gas is acquired by burning of natural gas with steam

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$$

- Catalyst is 'Fe' embedded in mixture of MgO, Al_2O_3, SiO_2

$$N_2 + 3H_2 \underset{400^0C}{\overset{Fe,200\ atm}{\rightleftharpoons}} 2NH_3 \qquad \Delta H = -92.46\ kj$$

- Equilibrium mixture has 35% by volume ammonia gas
- Ammonia gas is liquefied and dried with CaO
- 110 million tons of ammonia are synthesized in world
- 80 % used for production of fertilizers and some in manufacture of explosives, nylon, other polymers
- Its yield is maximized by;
  - Decreasing the temperature
  - Increasing the pressure
  - Continuous removal of ammonia

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -194\ kj$$

- Its yield is maximized by;
  - Decreasing the temperature
  - Increasing the pressure
  - Continuous removal of SO_3

pH and pOH, Kw, Ka, Kb, pKa pKb: [only for concept]

- **pH:** Negative log of hydrogen ion concentration ⇛ $pH = -\log[H^+]$
- **pOH:** Negative log of hydroxide ion concentration ⇛ $pOH = -\log[OH^-]$
- **pH = 7 (neutral)** **pH < 7 (acidic)** **pH > 7 (basic)**

(ionic prodcut of water) $K_w = [H^+][OH^-] = 10^{-14}$

$pK_w = pH + pOH = 14$

$pK_a + pK_b = pH + pOH = pK_w = 14$ **at 25^0C** ($-\log K_a = pK_a$, $-\log K_b = pK_b$)

Acidity ∝ Ka is acid dissociation constant **Basicity ∝Kb** is base dissociation constant

$K_a \propto 1/K_b$

$pK_a \propto$ 1/strength of acid $pK_b \propto$ 1/strength of base

Common ion Effect:

- Suppression of ionization of weak electrolyte by adding a strong electrolyte from outside having common ion
- **Examples:** $NaCl \rightleftharpoons Na^+ + Cl^-$

  $HCl \rightleftharpoons H^+ + Cl^-$
- Cl^- is the common ion and addition of HCl (strong electrolyte) results the precipitation of NaCl

  NH_4OH (weak) $\rightleftharpoons NH_4^+ + OH^-$

  NH_4Cl (strong) $\rightleftharpoons NH_4^+ + Cl^-$
- NH_4^+ is the common ion and this mixture is used for identification of basic radicals of 3rd group

  H_2S (weak) $\rightleftharpoons 2H^+ + S^{-2}$

  HCl (strong) $\rightleftharpoons H^+ + Cl^-$
- H^+ is the common ion and this mixture is used for identification of basic radicals of 2nd group

$$HF \rightleftharpoons H^+ + F^-$$
$$NaF \rightleftharpoons Na^+ + F^-$$

- F^- is the common ion and addition of NaF (strong electrolyte) results the suppression of HF

Features of Common ion Effect:

- ✓ It is the application of Le-Chatelier's principle
- ✓ Study the increase in concentration of product in form of common ions
- ✓ Addition of common ion always reverses the direction of reaction for weak electrolyte
- ✓ Term electrolyte is used instead of acid, base or salt
- ✓ Used in purification i.e. purification of NaCl using HCl
- ✓ Used in qualitative analysis (radical identification)
- ✓ Used to prepare Buffers

Buffer Solutions:

- ❖ The solutions which resist a change in their pH when small amount of acid or base being added
- ❖ Blood is a buffer with pH of 7.35
- ❖ **Acidic Buffer:**
  - Weak acid + its salt (which is made with strong base)
  - $CH_3COOH + CH_3COONa$ (best buffer when [Acid] = [Salt])
- ❖ **Basic Buffer:**
  - Weak base + its salt (which is made with strong acid)
  - $NH_4OH + NH_4Cl$ (best buffer when [Base] = [Salt])

Henderson Equation: [Example 5, Q 23]

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad\qquad pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

If [salt] = [acid] $\Rightarrow$ $pH = pK_a$ If [salt] = [base] $\Rightarrow$ $pOH = pK_b$

- If [salt] is 10 times greater than [acid], then $pH = pK_a + 1$
- If [salt] is 10 times lesser than [acid], then $pH = pK_a - 1$

Buffer Capacity: Capability of buffer to resist the change in its pH

Solubility: Amount of solute in 100 g of solvent to make a saturated solution at specific temperature

Solubility Product (Ksp):

- ❖ Product of the concentrations of ions raised to an exponent equal to the coefficient of the balanced equation
- ❖ For sparingly soluble salts
- ❖ Smaller the value of Ksp, lesser will be the dissociation

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x} \qquad\qquad Ksp = [A^{+y}]^x[B^{-x}]^y$$

$PbF_2 \rightleftharpoons Pb^{+2} + 2F^-$ $\quad\quad$ $Ksp = [Pb^{+2}][F^-]^2$

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+][Br^-]$	$5.0x10^{-13}$	CuS	$[Cu^{2+}][S^{2-}]$	$8x10^{-34}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$8.1x10^{-12}$	FeS	$[Fe^{2+}][S^{2-}]$	$6.3x10^{-18}$
AgCl	$[Ag^+][Cl^-]$	$1.8x10^{-10}$	Fe_2S_3	$[Fe^{3+}][S^{2-}]^3$	$1.4x10^{-85}$
AgI	$[Ag^+][I^-]$	$8.3x10^{-17}$	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	$1.6x10^{-39}$
Ag_2S	$[Ag^+]^2[S^{2-}]$	$8x10^{-48}$	HgS	$[Hg^{2+}][S^{2-}]$	$2x10^{-50}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	$3x10^{-34}$	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	$3.5x10^{-8}$
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}]$	$2x10^{-9}$	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	$6.3x10^{-10}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	$1.1x10^{-10}$	MnS	$[Mn^{2+}][S^{2-}]$	$3x10^{-11}$
CdS	$[Cd^{2+}][S^{2-}]$	$8.0x10^{-27}$	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	$1.6x10^{-5}$
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}]$	$3.3x10^{-9}$	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	$2.3x10^{-13}$
CaF_2	$[Ca^{2+}][F^-]^2$	$3.2x10^{-11}$	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	$1.6x10^{-8}$
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	$6.5x10^{-6}$	PbS	$[Pb^{2+}][S^{2-}]$	$8.0x10^{-28}$

❖ At least practice relation b/w Ksp and conc. of ions of different salts

Applications:

1. **Ksp is determined if solubility (S) is given [Example 6, Q.24]**
2. **Solubility (S) is determined if Ksp is given [Example 7, Q.25]**
   Relationship b/w Ksp and 'S' is written as when want to find 'S'

$$PbF_2 \rightleftharpoons Pb^{+2} + 2F^-$$
$$Ksp = (S)(2S)^2 = 4S^3$$